

# Low-Temperature, Anode-Supported High Power Density Solid Oxide Fuel Cells with Nanostructured Electrodes

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## Objectives

- To develop a theoretical model for nanostructured electrodes by taking into account charge transfer (activation) and mass transport (concentration) polarizations.
- To identify suitable materials for the cathode and anode, in addition to Sr-doped  $\text{LaMnO}_3$  (LSM) + yttria-stabilized zirconia (YSZ) and Ni + YSZ, respectively.
- To fabricate anode-supported cells with a nanostructured Ni + YSZ anode, a nanostructured LSM + YSZ cathode, and YSZ (as well as zirconia containing other stabilizers) electrolyte.
- To conduct a mechanical and thermo-mechanical analysis of anode-supported cells.
- To measure the electrochemical performance of cells with nanostructured electrodes.
- To conduct electrochemical tests, such as complex admittance spectroscopy, and current interruption on the cells.
- To characterize the electrode microstructure and analyze data in light of the model.

## Key Milestones

- Year 1: Conduct theoretical analysis of the effect of electrode microstructure on activation and concentration polarization.
- Year 2: Fabricate samples and cells with graded, nanostructured electrodes.
- Year 3: Conduct mechanical, electrochemical, and microstructural characterization of cells with nanostructured electrodes, and analyze the data.

## Abstract

**Theoretical Modeling and Microstructure of a High Performance Cell:** The theoretical and experimental work conducted has shown that with state of the art materials, namely YSZ for the electrolyte, Ni + YSZ for the anode, and LSM (or LSM + YSZ) as the cathode, the major cell losses are attributed to ohmic polarization principally due to the electrolyte, and electrode polarization principally due to the cathode. The electrolyte contribution can be lowered by fabricating cells comprising thin YSZ electrolyte film (~10 microns) supported on a porous Ni + YSZ anode. This approach now is by far the most commonly used. With this cell design, the principal loss is attributed to the cathode, and in particular to the cathode activation polarization. Theoretical work has also shown that in cathodes containing porous contiguous mixtures of an electrocatalyst, such as LSM, and an oxygen ion conductor, such as YSZ, the three phase boundaries (TPB) extend well into the cathode, in regions removed from the physically distinct cathode/electrolyte interface, and thereby substantially lower the cathodic polarization. This realization over the past few years has been instrumental in a shift away from single-phase LSM cathodes, such as those used in earlier work, to composite cathodes comprising mixtures of LSM and YSZ, or other similar materials.

Theoretical work has also demonstrated that electrode microstructure in the immediate vicinity of the electrode/electrolyte interface should be as fine as

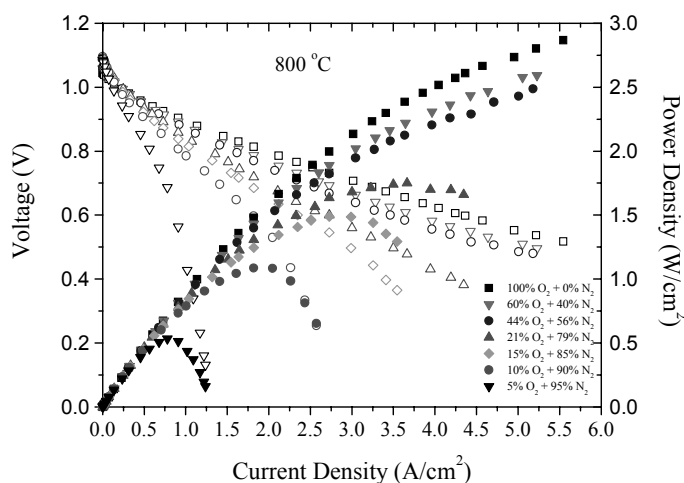
possible (nanostructured), which effectively increases TPB. At the same time, in regions away from the interface, the electrode structure should be coarse and highly porous in order to enhance gas transport and thereby lower concentration polarization. Thus, a high performance anode-supported solid oxide fuel cell (SOFC) has five layers: (1) A relatively thick (0.5 to 1 mm) porous Ni + YSZ anode support of a coarse microstructure and high porosity. Ni should be contiguous to ensure good electronic conductivity, and of course the porosity must be contiguous; (2) a very fine, porous, Ni + YSZ (or possibly Ni + doped ceria), electrocatalytic layer (or interlayer) of a thickness  $\sim 10$ –20 microns, wherein both phases are contiguous, and so is the porosity; (3) a thin ( $\sim 10$  microns) dense layer of YSZ, or another suitable electrolyte; (4) a fine, porous electrocatalytic layer (interlayer) containing the electrocatalyst (e.g. LSM or Sr-doped  $\text{LaCoO}_3$  (LSC)) and an oxygen ion conductor (e.g. YSZ or doped ceria), both being contiguous along with the porosity, of a thickness on the order of 10 to 30 microns; and (5) a highly porous and coarse layer of an electronic conductor, such as LSM of a thickness on the order of 50 to 100 microns. Figure 1 shows a scanning electron micrograph (SEM) of a typical anode-supported cell fabricated in our laboratory. Cells of this typical microstructure, using various electrocatalysts and their morphologies, are routinely fabricated in our laboratory by conventional processing methods.

**Electrochemical Testing of Cells: The Effect of Oxidant Composition:** Electrochemical testing consists of evaluating cell performance, namely voltage vs. current density, as a function of temperature at various oxidant and fuel compositions. The ohmic contribution is obtained by current interruption. The majority of measurements were conducted at  $800^\circ\text{C}$ , with humidified hydrogen as fuel and  $\text{O}_2$ - $\text{N}_2$  mixtures as oxidant. The oxidant composition was varied between  $\sim 100\%$   $\text{O}_2$  to  $\sim 5\%$   $\text{O}_2 + \sim 95\%$   $\text{N}_2$ , which allowed for the study of the effect of inert gas ( $\text{N}_2$ ) on cell performance. There are two factors, which influence the cell performance: (a) Cathodic *concentration* polarization, which is a function  $\text{O}_2$  concentration in the oxidant, and parameters related to the cathode (porosity, pore size, thickness, etc.), and (b) Cathodic *activation* polarization, which is a function of the partial pressure of

oxygen in the cathode interlayer. Figure 2 shows performance curves of a cell at  $800^\circ\text{C}$  for several oxidant compositions. Note power density as high as  $\sim 2.9 \text{ W/cm}^2$  could be realized in  $\sim 100\%$   $\text{O}_2$ ,  $\sim 1.7 \text{ W/cm}^2$  in air, however, only about  $\sim 0.5 \text{ W/cm}^2$  in an oxidant containing  $\sim 5\%$   $\text{O}_2$ . Three important observations can be made based on this study: (a) In  $\sim 100\%$   $\text{O}_2$ , very high performance was achieved, implying that the *anode* concentration polarization was not limiting, even at current densities exceeding  $5 \text{ A/cm}^2$ , despite its large thickness; (b) cathode performance is excellent in  $\sim 100\%$   $\text{O}_2$ ; and (c) cathode performance is less than satisfactory in oxygen-depleted oxidant, implying further improvements in the cathode are needed.



**Figure 1:** An SEM micrograph of a typical cell showing four layers. The coarse cathode layer is not present in this cell.

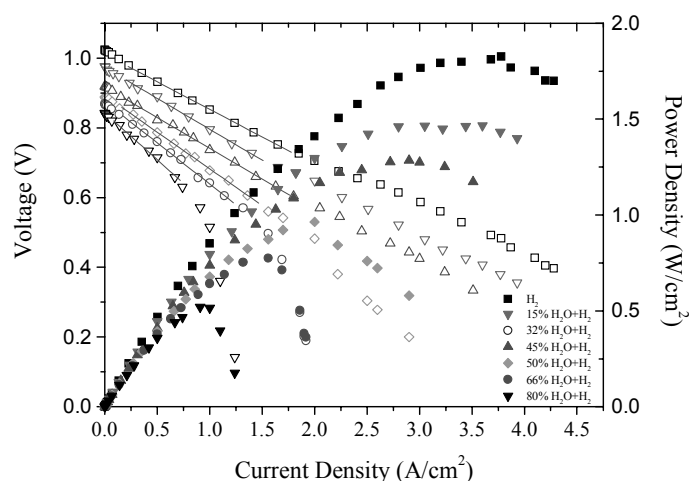


**Figure 2:** Performance curves of a cell at  $800^\circ\text{C}$  as a function of oxidant composition.

**The Effect of Fuel Composition:** In a practical fuel cell, the fuel composition varies over the surface of the cell, and throughout the stack, because inlet fuel is rich in  $H_2$  (or in  $H_2$  and CO), while the exhaust fuel stream is depleted in  $H_2$  (or in  $H_2$  and CO). The performance of a cell is usually not uniform over the entire surface. It is thus necessary to examine the cell performance as a function of fuel utilization. In a laboratory-sized cell of 1 to 2  $cm^2$  of active area, this is usually difficult to do. An alternative approach is to investigate cell performance as a function of fuel composition, wherein the fuel composition is varied, by using laboratory-sized cells. Figure 3 is an example of such a test, where the fuel composition was varied between  $\sim 100\%$   $H_2$  (with trace amount of  $H_2O$ ) and  $\sim 20\%$  +  $\sim 80\%$   $H_2O$ . The cell was tested at  $800^\circ C$  with air as the oxidant. Note that the maximum power density ranges between  $\sim 1.8$   $W/cm^2$  for  $\sim 100\%$   $H_2$ , and  $\sim 0.5$   $W/cm^2$  for  $\sim 20\%$   $H_2$  +  $\sim 80\%$   $H_2O$ . The observed differences have been interpreted by taking into account gas transport through the porous anode, and the associated concentration polarization.

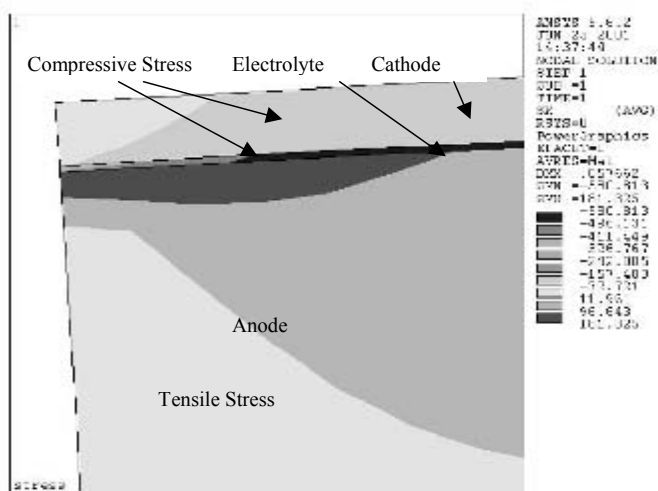
**Thermo-Mechanical Analysis of Anode-Supported Fuel Cells:** As the three components of a fuel cell—namely, anode, electrolyte, and cathode—are physically bonded to each other, stresses can arise due to differences in coefficients of thermal expansion. In anode-supported SOFC of conventional materials, the anode (Ni + YSZ) has a greater coefficient of thermal expansion than the electrolyte (YSZ). Thus, the YSZ electrolyte is in biaxial compression, while the anode is in biaxial tension. Since the anode thickness is much larger than the electrolyte, the magnitude of tension in the anode is much smaller than the magnitude of compression in the electrolyte. Thus, tendency for anode cracking is minimal (low tension), and the electrolyte should not crack (since it is in compression). However, the delamination of the YSZ electrolyte along the electrolyte/anode interface is possible, and must be evaluated, since this is the likely mode of cell failure under thermo-mechanical stresses. The cathode thermal expansion can vary over a wide range, depending upon the choice of the cathode material. With LSM + YSZ as the cathode, its thermal expansion is close to that of the electrolyte YSZ. If, on the other hand, LSC + samaria-doped ceria (SDC) is used as the cathode, its coefficient of thermal expansion is closer to the anode. The

conditions under which delamination can occur depend on a number of parameters. Finite element analysis was conducted to elucidate the role of thermal expansion mismatch stresses. Figure 4 shows the results of a typical finite element calculation on the three-component (cathode (positive)-electrolyte-anode (negative) - PEN) structure. Figure 5 shows the calculated elastic energy release rate for a delamination crack along the anode-electrolyte interface, as well as along the cathode-electrolyte interface, as a function of cathode thickness, for Ni + YSZ anode of 1 mm thickness, YSZ electrolyte of 10 microns thickness, and LSM + YSZ cathode of varying thickness.

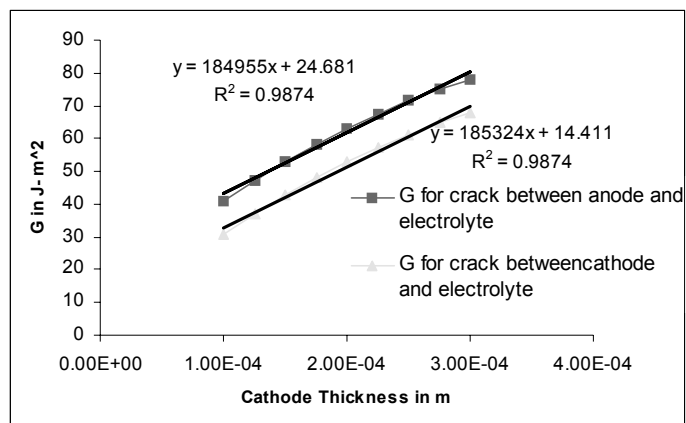


**Figure 3:** Performance curves of an anode-supported cell at various concentrations of  $H_2$  in  $H_2 + H_2O$  mixtures as fuel. Tests were conducted at  $800^\circ C$  with air as the oxidant.

The calculations show that as the cathode thickness increases, tendency for delamination increases. Thus, cathode thickness should be no greater than necessary. The general conclusions of the calculations are as follows: (a) The tendency for delamination increases with increasing electrolyte thickness, thus, the electrolyte (YSZ) film should be as thin as possible; and (b) Tendency for delamination is higher if the cathode is matched in thermal expansion coefficient with the electrolyte, rather than the anode. Thus, in anode-supported cells, the cathode should be matched with the anode, and not the electrolyte. This is an important difference from the Siemens-Westinghouse design, in which it is preferable to match the cathode with the electrolyte.



**Figure 4:** The results of a finite element calculation on the anode-electrolyte-cathode (PEN) structure. Color code shows the magnitudes and signs of the stresses ( $\sigma_{xx}$ ).



**Figure 5:** Plots of the elastic energy release rate for delamination crack along the anode-electrolyte interface and cathode-electrolyte interface, as a function of cathode thickness

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Two more papers have been published in conference proceedings, and two more papers will be written for publication over the next few months.